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(54) **Electrochemical cells**

(57) An electrochemical cell (10) particularly for sensing hydrogen in solution or gases comprises a generally cylindrical hollow body (11) with opposed end caps (13, 15) secured thereto by bolts (16), the proximal surfaces (13A, 15A) of the end caps (13, 15) being plane-parallel and respectively clamping an electrode assembly (14, 17) against the ends of the body (11). Each electrode assembly (14, 17) includes a planar electrode member (14A, 17A) and an O-ring seal (14D, 17D), seal (17D) being interposed between electrode members (17A) and surface (15A) to establish a chamber (18) communicating with which through the end cap (15) are inlet and outlet passageways (15B, 15C) through which a gaseous sample to be tested is transported. Cell (10) further includes a reference electrode assembly (20) formed in the bore of a hollow bolt screw threadedly received in a radially extending bore 11D in the hollow body 11.

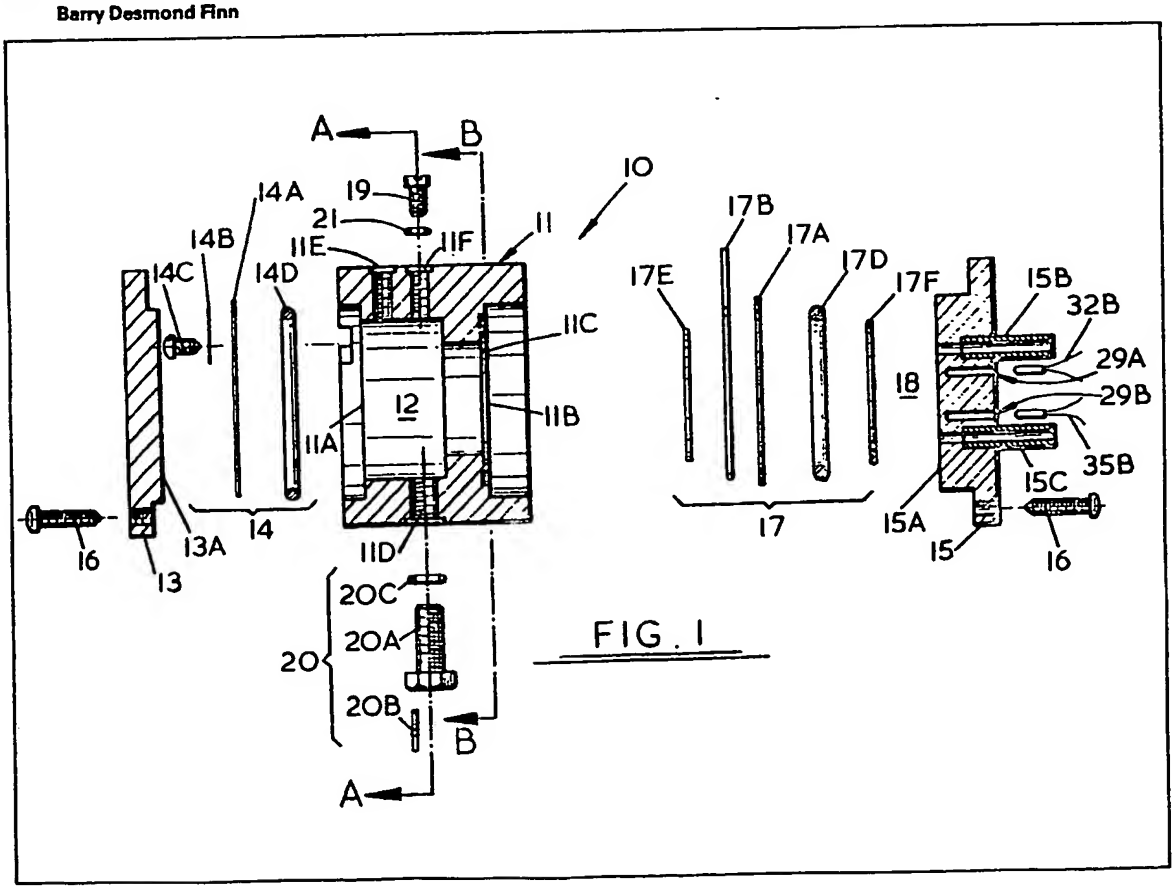

FIG. 1

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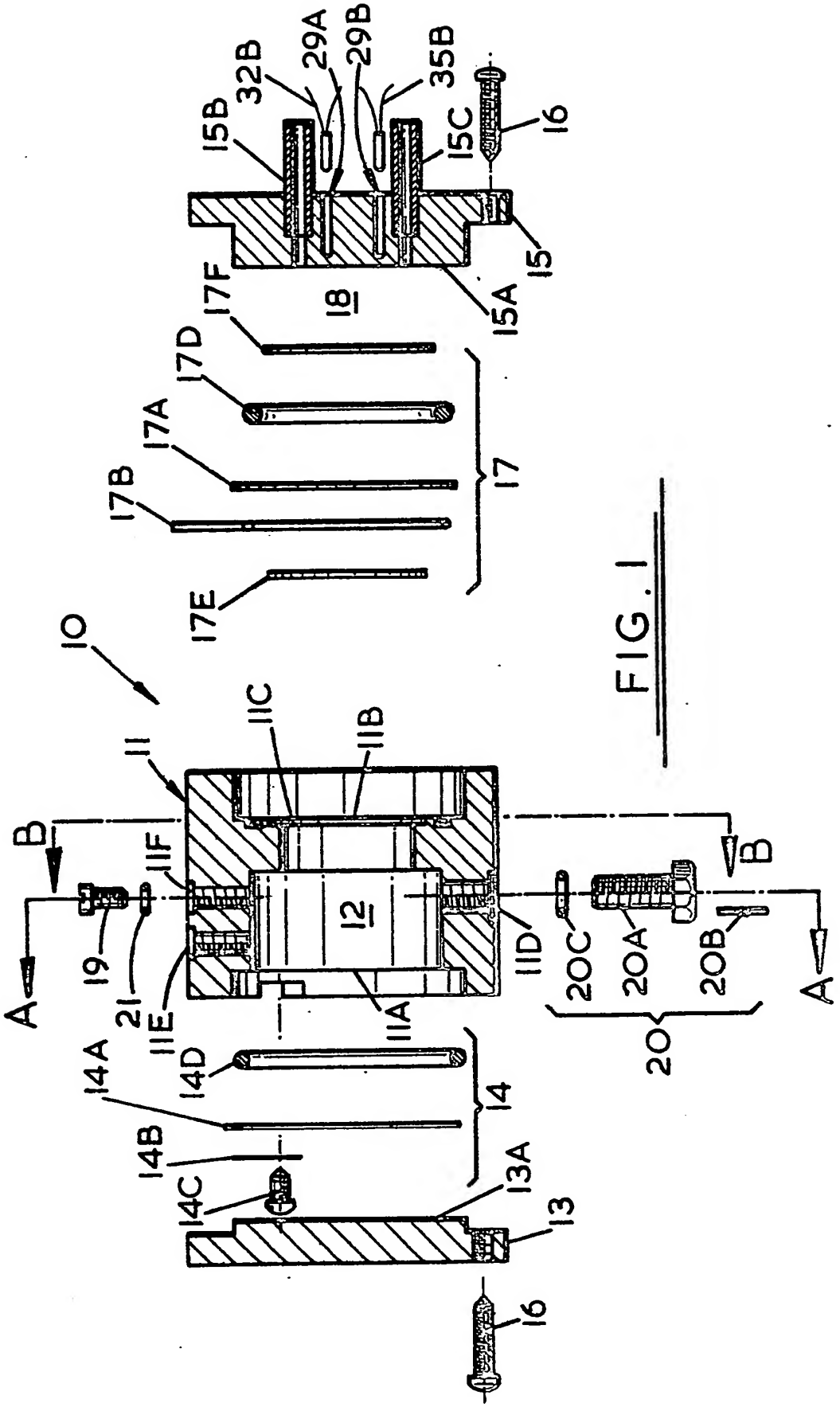
10
11
11C
11B
11F
11E
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12
B
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19
21
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20A
20B
14
14A
14D
14B
14C
13
13A
16
17
17F
17D
17A
17B
17E
18
15
15A
15B
15C
32B
29A
29B
35B

FIG. 1

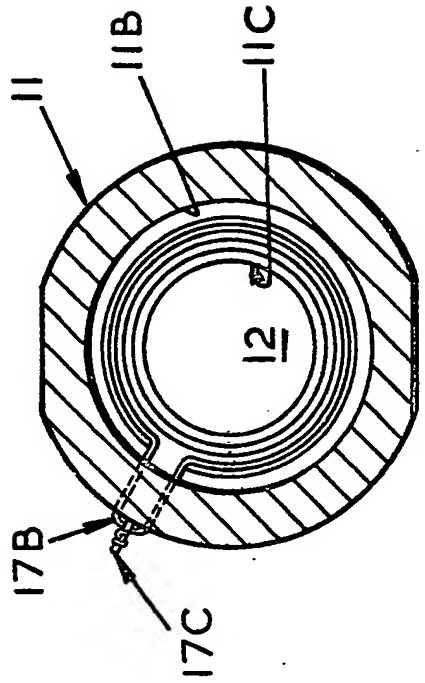

FIG. 3

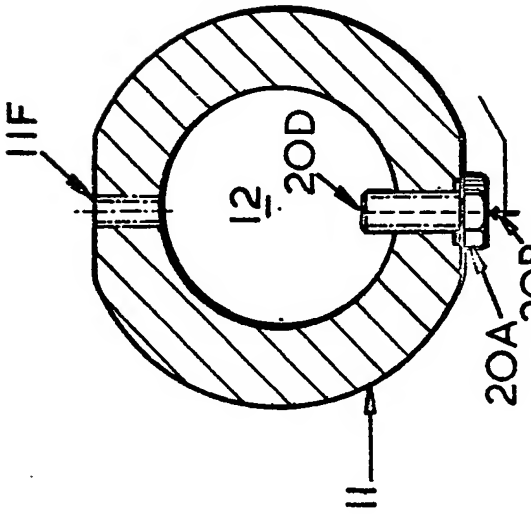

FIG. 2

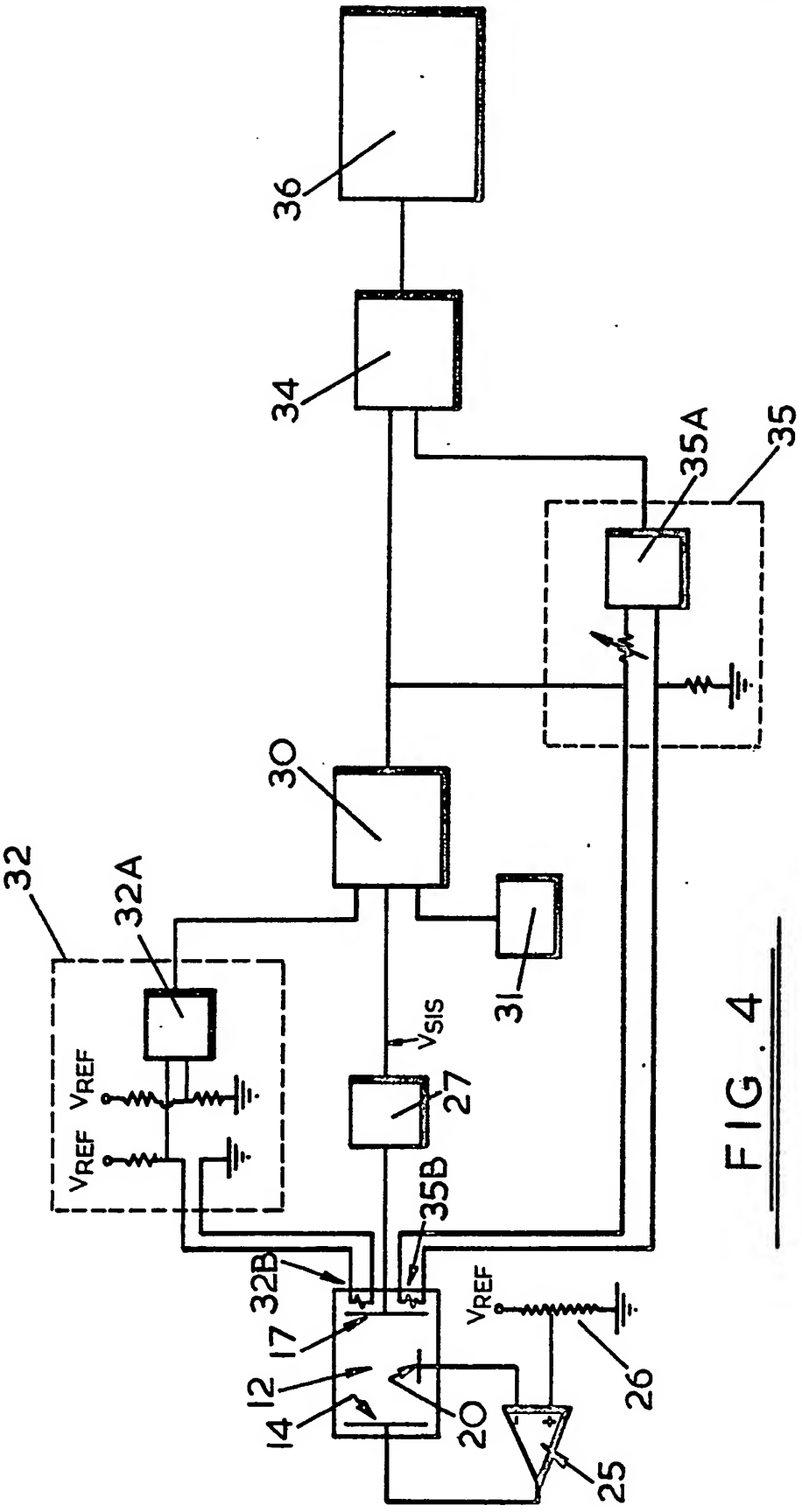
36
34
35A
35
30
32
32A
31
V_{SIS}
27
V_{REF}
V_{REF}
35B
32B
17
12
14
20
V_{REF}
26
25

FIG. 4

SPECIFICATION

Electrochemical cells

This invention relates to electrochemical cells, particularly such cells capable of sensing hydrogen in solution or in gaseous mixture.

Various forms of electrochemical cells are already known and have been extensively described in the literature but we have found that these cells when tested for their ability to monitor hydrogen in a gaseous mixture have required individual adjustments to high tolerances throughout their working lives and accordingly have not been susceptible to production manufacturing techniques.

According to the present invention there is provided an electrochemical cell comprising an electrolyte housing defined by a generally cylindrical hollow body with opposed end caps releasably secured thereto by bolts, the proximal surfaces of said end caps being substantially plane-parallel and each peripherally clamping an electrode assembly against a respective annular shoulder of the hollow body, each electrode assembly comprising a substantially planar electrode member and an O-ring seal, one electrode member being a counter electrode and the other being a working electrode, wherein the working electrode is spaced from the adjoining end cap by the pertaining O-ring seal whereby a chamber is formed between the working electrode and the adjoining end cap and inlet and outlet passageways are provided in said adjoining end cap for flow of test fluid into and out of said chamber, a reference electrode being formed in the bore of a hollow bolt screw-threadedly received in a radially-extending bore in the hollow body with an O-ring seal clamped in a counter-bore against the hollow body by the head of the hollow bolt.

Preferably the hollow body and each end cap is made of an inert plastics material such as polymethyl-methacrylate.

Preferably the counter electrode comprises a lead disc having a lead dioxide coating in contact with the electrolyte and electrical contact with the disc is by way of a solder tag secured by a screw to said body.

Preferably the reference electrode comprises a mercury-coated platinum wire embedded in a paste-like amalgam of mercury and mercurous sulphate within the bore of the hollow bolt, electrical contact with the platinum wire being by way of a solder pin bonded to the bolt.

Preferably the working electrode comprises a metallised membrane for example a PTFE substrate coated on the surface thereof proximal the counter electrode firstly with a thin layer of gold and thereafter with a thin layer of platinum. Conveniently electrical contact with the working electrode is by way of an encircling gold wire abutting the platinum coating and secured to a solder pin bonded to the body. Conveniently the electrode assembly of which the working electrode forms part comprises a pair of porous polymeric discs, one on either side of the working electrode, and for example made of 'Vyon' (Registered Trade Mark). The polymeric disc adjacent the counter electrode may be solid or apertured.

Preferably the end cap adjoining the working electrode houses a pair of thermistors extending into close proximity with said chamber whereby to monitor the temperature of the test fluid the thermistors being electrically connected in circuit with said reference, counter and working electrodes.

Preferably the mercury coating on the platinum wire of the reference electrode is effected electrochemically and the metallic coatings of the working electrode are effected by cool sputtering. Preferably the metallic coatings of the working electrode are each thickness-monitored to provide a coating thickness accurate to ± 10 Angstrom. Preferably the gold coating is 1000 Angstroms thick and the platinum coating is 3000 Angstroms thick.

Preferably the lead dioxide coating of the counter electrode is effected in situ by reverse polarisation of the counter and working electrode members, the electrolyte being 0.1M sulphuric acid and the working electrode being exposed to atmosphere as the test fluid. With this arrangement a lead dioxide coating is formed on the lead disc.

Preferably the reference, working and counter electrodes are connected in an electrical circuit, during use of the cell as a hydrogen monitor, such that the counter electrode voltage is maintained at a constant level during the working life of the cell.

It will now be evident that the cell according to the present invention is relatively simple to manufacture in that it comprises relatively few components but these are arranged to render the electrolyte housing leak-proof throughout the life of the cell and with the end caps being releasably secured by bolts the end caps can be secured to the body without shearing the pertaining electrode members and can be released so as to replace the electrode members at the end of their useful lives. Furthermore the electrical connections to the three electrodes provide excellent and long lasting electrical contact which is also physically robust.

An embodiment of the present invention will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 is an exploded side view of a cell in accordance with the present invention;

Figure 2 is a section on A-A in Figure 1;

Figure 3 is a section on B-B in Figure 1; and

Figure 4 is an electrical wiring diagram for the cell.

The cell 10 illustrated in exploded form in Figure 1 comprises a generally cylindrical hollow body 11 with opposed end caps 13, 15 secured thereto by bolts 16. Bolts 16 may be six or eight in number for each end cap but only one for each end cap has been illustrated in the interests of clarity. Surface 13A of end cap 13 is plane parallel with surface 15A of end cap 15 and surface 13A clamps electrode assembly 14 against annular shoulder 11A of body 11 whilst surface 15A clamps electrode assembly 17 against annular shoulder 11B of body 11.

Electrode assembly 14 comprises a substantially planar electrode member 14A in the form of a lead disc having a lead dioxide coating facing shoulder 11B, a solder tag 14B making electrical contact with the disc 14A and secured to body 11 outside the annular shoulder 11A by means of a screw 14C, and

an O-ring seal 14D. Accordingly assembly 14 functions as a counter electrode and is sealingly secured within the cell 10.

Electrode assembly 17 comprises a substantially planar electrode member 17A in the form of a metallised membrane electrical contact therewith being provided by an encircling gold wire 17B the free ends of which are secured to a single solder pin 17C (see Figure 3) secured to the body 11, the surface of the electrode member 17A adjacent shoulder 11A is protected by an un-apertured porous polymeric disc 17E which seats in an annular recess 11C within body 11, whilst the other surface of member 17A is protected by an apertured porous polymeric disc 17F and is spaced from surface 15A of cap 15 by an O-ring seal 17D so that a small sample test chamber 18 is formed thereat and into which the gaseous sample to be tested is transported by way of inlet and outlet passageways 15B, 15C formed in end cap 15. It will now be evident that assembly 17 functions as a working electrode and is sealingly secured within the cell 10.

The cell 10 further comprises a reference electrode assembly 20 in the form of a mercury-coated platinum wire 20D (see Figure 2) embedded in a paste-like amalgam of mercury and mercurous sulphate within the bore of a hollow bolt 20A, electrical contact with the platinum wire being by way of a solder pin 20B secured to the bolt head, the bolt 20A being threadedly received in an aperture 11D formed in the body 11 and the bolt head seating against an O-ring seal 20C to render the electrode 20 leak proof.

When the three electrodes are fitted to the body 11 the hollow interior forms an electrolyte housing 12, electrolyte being inserted by way of fill holes 11E, 11F each having a screw-threaded plug 19 and associated O-ring seal 21 whereby the cell 10 is rendered completely sealed when in use (only one plug 19 and seal 21 being illustrated in the interests of clarity).

The materials used as the components of the cell 10 are as previously described and the manufacture of certain individual components is as previously specified.

When the completed cell 10 is assembled and the counter electrode conditioned to provide the lead dioxide coating thereon the cell is electrically connected in the circuit illustrated in Figure 4 for normal usage. Thus, the counter electrode 14A has its voltage established by differential amplifier 25 one input of which is connected to an adjustable reference voltage source 26 and the other input of which is connected to the reference electrode 20D. In normal operation the counter electrode voltage is constant and the reference electrode current is likewise constant. The working electrode 17A produces a current signal which is applied to a voltage converting amplifier 27 the output of which provides a signal voltage Vsig.

The signal Vsig is applied to a summation amplifier 30 which receives further inputs from a zero adjust circuit 31 and from a first temperature compensation circuit 32. The output of amplifier 30 is then applied to a gain control amplifier 34 which further receives a signal from a second temperature compensation circuit 35 and the output of amplifier 34 drives a read-out 36 which may be a digital display or a print-out.

The first compensation circuit 32 comprises a comparator 32A the two inputs of which are derived from respective potential dividers fed from reference voltages and one of the potential divides incorporates a thermistor 32B which is physically located in a pocket 29A in end cap 15 such that the thermistor 32B is sensitive to the temperature of the sample in the test chamber 18.

The second compensation circuit 35 comprises a differential amplifier 35A the two inputs of which are each fed from the output of amplifier 30 by way of respective resistors one of which is a thermistor 35B which is physically located in a pocket 29B in end cap 15 such that thermistor 25B is sensitive to the temperature of the sample in the test chamber 18.

In order to isolate the entire cell 10 from the effects of ambient temperature variations, other than that necessary because of the existence of the test chamber 18, the cell 10 is itself housed in a thermally insulating jacket.

CLAIMS

1. An electrochemical cell comprising an electrolyte housing defined by a generally cylindrical hollow body with opposed end caps releasably secured thereto by bolts, the proximal surfaces of said end caps being substantially plane-parallel and each peripherally clamping an electrode assembly against a respective annular shoulder of the hollow body, each electrode assembly comprising a substantially planar electrode member and an O-ring seal, one electrode member being a counter electrode and the other being a working electrode, wherein the working electrode is spaced from the adjoining end cap by the pertaining O-ring seal whereby a chamber is formed between the working electrode and the adjoining end cap and inlet and outlet passageways are provided in said adjoining end cap for flow of test fluid into and out of said chamber, a reference electrode being formed in the bore of a hollow bolt screw-threadedly received in a radially-extending bore in the hollow body with an O-ring seal clamped in a counter-bore against the hollow body by the head of the hollow bolt.

2. An electrochemical cell as claimed in claim 1, wherein the counter electrode comprises a lead disc having a lead dioxide coating in contact with the electrolyte and electrical contact with the disc is by way of a solder tag secured by a screw to said body.

3. An electrochemical cell as claimed in either preceding claim, wherein the reference electrode comprises a mercury-coated platinum wire embedded in a paste-like amalgam of mercury and mercurous sulphate within the bore of the hollow bolt, electrical contact with the platinum wire being by way of a solder pin bonded to the bolt.

4. An electrochemical cell as claimed in any preceding claim, wherein the working electrode comprises a metallised membrane coated on the surface thereof proximal the counter electrode firstly with a thin layer of gold and thereafter with a thin

layer of platinum.

5. An electrochemical cell as claimed in claim 4, wherein electrical contact with the working electrode is by way of an encircling gold wire abutting the platinum coating and secured to a solder pin bonded to the body.

6. A electrochemical cell as claimed in claim 4 or claim 5, wherein the electrode assembly of which the working electrode forms part comprises a pair of porous polymeric discs, one on either side of the working electrode.

7. An electrochemical cell as claimed in any preceding claim, wherein the end cap adjoining the working electrode houses a pair of thermistors extending into close proximity with said chamber whereby to monitor the temperature of the test fluid the thermistors being electrically connected in circuit with said reference, counter and working electrodes.

8. An electrochemical cell as claimed in any preceding claim, wherein the reference, working and counter electrodes are connected in an electrical circuit, during use of the cell as a hydrogen monitor, such that the counter electrode voltage is maintained at a constant level during the working life of the cell.

9. An electrochemical cell as claimed in claim 1, and substantially as hereinbefore described with reference to Figures 1-4 of the accompanying drawings.

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